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<p>The NMR and Raman techniques were used to investigate the hydrolysis and condensation mechanism in $B_2O_3-SiO_2$; $Al_2O_3-SiO_2$; and $Na_2O-Al_2O_3-SiO_2$ systems. The solid state NMR techniques were employed together with BET methods to follow the thermal treatment of the gels. In addition to the NMR and Raman techniques, the SANS method was employed to study the effects of fluoride anion catalyst on the sol-gel process involving TMOS.</p> <p>High pressure NMR studies of the dynamic structure of the highly viscous liquids focused on three projects: i) the self-diffusion behavior, and the applicability of hydrodynamic equations at the molecular level for a model lubricant - 2-ethylhexylbenzoate; ii) the effect of the dipole moment on the hydrodynamic behavior of highly polar fluids; iii) the effect of molecular flexibility on the relationship between molecular properties and shear viscosity at extreme conditions of pressure. Boron oxides, Silicon dioxide</p>					
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PRINCIPAL INVESTIGATOR: Dr. Jiri Jonas
Department of Chemistry
School of Chemical Sciences
University of Illinois
Urbana, IL 61801

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SENIOR RESEARCH PERSONNEL:	Dr. I. Artaki	Dr. N. A. Walker
	Dr. R. Frattini	Dr. R. Winter
	Dr. J. S. Holmgren	Dr. T. W. Zerda
	Dr. S. Plesko	

JUNIOR RESEARCH PERSONNEL:	S. T. Adamy	A. D. Irwin
	J.-B. Chan	M. L. Phillips
	D.-W. Hua	M. J. Welsh

PUBLICATIONS:

"Kinetics and Mechanism of Sol-Gel Polymerization," Jiri Jonas, Ultrastructure Processing of Ceramics, Glasses and Composites, Ed. L. L. Hench and D. R. Ulrich (J. W. Wiley, N.Y.), 1986.

"NMR, Raman Study of the Effect of Formamide on the Sol-Gel Process," I. Artaki, M. Bradley, T. W. Zerda, J. Jonas and G. Orzel and L. L. Hench, Ultrastructure Processing of Ceramics, Glasses and Composites, Ed. L. L. Hench and D. R. Ulrich (J. W. Wiley, N.Y.), 1986.

"Study of Polymerization Processes in Acid and Base Catalyzed Silica Sol-Gels," T. W. Zerda, I. Artaki and J. Jonas, J. Non-Crystalline Solids, 81, 365 (1986).

"Solvent Effects on the Condensation State of the Sol-Gel Process," I. Artaki, T. W. Zerda and J. Jonas, J. Non-Crystalline Solids, 81, 381 (1986).

"High Pressure in Chemical Kinetics," J. Jonas in Proc. X AIRAPT International High Pressure Conference on Research in High Pressure Science and Technology, held in Amsterdam, July 1985, Physica, 139 & 140B, 673 (1986).

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"Thermotropic Ionic Liquid Crystals VI. Structural Parameters of Solid and Liquid Crystal Phases of Anhydrous Short-Chain Sodium Alkanoates," M. L. Phillips and J. Jonas, Liquid Crystals, 2, 335 (1987).

"Thermotropic Ionic Liquid Crystals. VII. Calculation of Sodium-23 Quadrupole Coupling Constants in Lamellar Phases of Sodium Alkanoates," M. L. Phillips and J. Jonas, J. Chem. Phys., 86, 4294 (1987).

"Nuclear Magnetic Resonance and Laser Scattering Techniques at High Pressure," Jiri Jonas, R. van Eldik and J. Jonas Eds., High Pressure Chemistry and Biochemistry, pp. 193-235 (1987), NATO ASI, Series C, Vol. 197.

"Solid State ^{29}Si NMR Study of Polycondensation During Heat Treatment of Sol-Gel Derived Silicas," A. D. Irwin, J. S. Holmgren and J. Jonas, Materials Letters, 6, 25 (1987).

"NMR Studies of Mixed Alkoxide Systems," J. Jonas, A. D. Irwin and J. S. Holmgren, Third International Conference on Ultrastructure Processing of Ceramics, Glasses and Composites, Ed. J. D. Mackenzie and D. R. Ulrich (J. W. Wiley, NY), 1987.

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"Self-Diffusion in the Compressed, Highly Viscous Liquid 2-Ethylhexyl Benzoate," N. A. Walker, D. M. Lamb, S. T. Adamy, J. Jonas, and M. P. Dare-Edwards, Journal of Phys. Chem., 92, 3675 (1988).

" ^{27}Al and ^{29}Si NMR Study of Sol-Gel Derived Aluminosilicates and Sodium Aluminosilicates," A. D. Irwin, J. S. Holmgren and J. Jonas, Journal of Materials Science, 23, 2908 (1988).

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ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

An improved molecular level understanding of the sol-gel process for preparing glasses represented the main goal of the research supported by this grant. In addition, the fundamental relationship between the molecular properties and macroscopic properties of highly viscous fluids was investigated. As a continuation of our earlier efforts, a further development of unique NMR and laser Raman scattering instrumentation to permit measurements of various disordered materials under extreme conditions of pressure and temperature was also pursued.

The NMR techniques used to investigate the sol-gel process involved both the high resolution NMR solution methods and the solid state techniques such as magic angle spinning and cross polarization. The hydrolysis and condensation mechanisms were studied in the B_2O_3 - SiO_2 , Al_2O_3 - SiO_2 and Na_2O - Al_2O_3 - SiO_2 sol-gel systems. The solid state NMR techniques together with BET methods were employed to follow the thermal treatment of the gels. In addition to the NMR and Raman techniques, small angle neutron scattering was used to investigate the effect of the fluoride anion catalyst on the sol gel process involving TMOS. Viscosity, SANS, NMR, fluorescence polarization, and static and dynamic high scattering techniques have recently been employed to investigate the sol-gel transition in TMOS. A theoretical analysis of the experimental data is in progress.

The high pressure NMR studies of the dynamic structure of the highly viscous liquids focused on three projects: i) the self-diffusion behavior and the applicability of hydrodynamic equations at the molecular level for a model lubricant 2-ethylhexylbenzoate; ii) the effect of dipole moment on the hydrodynamic behavior of highly polar fluids; iii) the effect of molecular flexibility on the relationship between molecular properties and shear viscosity at extreme conditions of high pressure.

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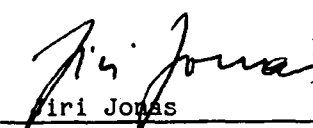



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 PRINCIPAL INVESTIGATOR
Name: Piri Jonas Department: Chemistry
Title: Professor Address: 166 Roger Adams Lab
 Telephone No.: (217) 333-2572

University of Illinois

1209 West California

Urbana, Illinois 61801

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1. Unique Character of Our Research Effort

There are several specific aspects of our work which make our research efforts unique. First, about 18 years ago we started our measurements on liquids using pressure as an experimental variable because we realized that only by separating the effects of density and temperature on the molecular motions one can unravel the details of the dynamic structure of liquids and other disordered materials. Therefore, we developed unique NMR instrumentation which allowed us to carry out the NMR experiments on various disordered systems over a wide range of pressures and temperatures. There is currently no other laboratory in the U.S.A. and abroad with comparable performance features of the experimental NMR high pressure setup. Both high resolution NMR solution techniques and high resolution solid-state NMR techniques, including magic-angle-spinning and cross polarization are used in our laboratory. Second, our research group is the only one which used two powerful techniques - NMR and also laser Raman scattering on a specific material. Clearly, this approach results in a significant synergistic effect. We have recently started using infrared, static and dynamic light scattering, and small angle neutron scattering techniques in our studies of the sol-gel process. In order to fully exploit the NMR or Raman data our group also measures more mundane but necessary properties such as PVT, diffusion and shear viscosities. Third, we have adopted a systematic approach in our studies, which approach is a prerequisite for successful solution of the complex problem of liquids, gels, glasses and polymers. Fourth, our experiments are always conceived with a specific goal of either testing current theories or providing new results which serve as a basis for developing new theoretical models.

2. Research Accomplishments Under Grant AFOSR 85-0345

2.1 Molecular Understanding of the Sol-Gel Process

After our initial NMR and Raman studies, our studies focused on mixed alkoxide systems. The investigation of the sol-gel process as a method for preparing multicomponent glasses and ceramic powders has been motivated by the possibility of producing very homogeneous products at temperatures much lower than those required to melt the constituent oxides. Such a homogeneity has been presumed to arise from chemical cross-polymerization between different alkoxides in solution. In practice however, one cannot simply mix the different alkoxides in the desired ratios and hope to prepare homogeneous materials. Different alkoxides hydrolyze at much different rates, and this kinetic incompatibility often leads to the precipitation of the faster hydrolyzing component(s). In some cases selective hydrolysis can occur, leading to the preferential polymerization of one component and resulting in a heterogeneous product. Since homogeneity of sol-gel derived materials is of prime importance, steps must be taken to avoid precipitation and self-polymerization. Toward this end, our studies aimed at gaining insight into the complex chemistry of multicomponent alkoxide sol-gel systems. Such chemical understanding should lead to reproducibility in sample preparation and enable the production of higher quality sol-gel derived materials.

The second main projects dealt with the effect of the fluoride anion catalyst on the sol-gel process involving TMOS. NMR, Raman and small angle neutron scattering techniques together with BET techniques were used to characterize the structural evolution of sol-gel systems catalyzed by the fluoride anion. In addition, a systematic study of the gelation process was started by using a host of macroscopic and microscopic techniques.

Our spectroscopic and chemical expertise, (NMR, IR, Raman, B.E.T.), coupled with our unique experimental capabilities (extreme conditions of temperature and pressure) placed us in a very good position to perform these studies.

2.11 $B_2O_3-SiO_2$

For borosilicate sol-gel systems, it has been established that the boron alkoxide hydrolyzes very rapidly, and must be added only after prehydrolysis of the silicon alkoxide. Using ^{11}B and ^{29}Si NMR as well as infrared spectroscopy, we have shown that although some borosiloxane ($=B-O-Si\equiv$) linkages are formed in solution, their concentration diminishes toward gelation due to re-hydrolysis to form boric acid. Borosiloxane units are not stable in these solutions containing excess water and alcohol. The boric acid does, however, condense to form borosiloxane units upon thermal treatment of dried gels. A small amount of self condensation also occurs to form $=B-O-B=$ groups, which do not convert to $=B-O-Si\equiv$ upon heating. We have investigated this system over a wide range of compositions and conditions (acid and base catalysis, various methods of prehydrolysis, etc.) and have shown thermal treatment of the dried gels to be the critical stage at which homogeneity is obtained, and have interpreted our results in terms of the molecular level processes occurring during each stage of the process.

A new method for the preparation of borosilicate glasses was also described. This method, which involves anhydrous addition of BX_3 ($X = F, Cl$) to silica xerogels, minimizes the boron loss which is normally associated with the preparation of borosilicate glasses by the sol-gel route. Spectroscopic evidence (IR, NMR) suggests that the BX_3 ($X = F, Cl$) reacts with surface hydroxyl groups in the xerogel to form $X_2B-O-Si\equiv$ linkages. Thermal treatment of these gels leads to full incorporation of boron into the silica network. The borosilicate glasses prepared in this way are analogous to those prepared by the more conventional sol-gel route.

2.12 $Al_2O_3-SiO_2$ and $Na_2O-Al_2O_3-SiO_2$

Aluminosilicate and sodium-aluminosilicate gels are quite difficult to prepare in aqueous/alcoholic media due to the tendency of aluminum alkoxides to dimerize in these environments, resulting in precipitation from the sol. Because such dimers have low solubilities, their formation leads eventually to phase separated powders. There is a further problem with product reproducibility. We have developed procedures to successfully deal with these problems. For example, the insolubility of aluminum dimers may be overcome by using a large excess of a bulky alcohol (e.g. isopropanol), which minimizes the formation of dimers by steric hindrance, and helps solvate those dimers which do form. Rapid gelation (1-2 days) may be achieved by pumping off the excess solvent under vacuum.

For the preparation of $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ gels, we have developed a procedure which allows for the preparation of homogeneous gels over a wide range of compositions. This route involves the preparation of a double alkoxide of sodium and aluminum, and the addition of this double alkoxide to a prehydrolyzed solution of silicon alkoxide.

2.13 Solid State NMR Studies

Since March 1987, when the solid state accessory of the new NMR spectrometer system was installed in our laboratory, we have carried out several studies using magic angle spinning (MAS) and MAS with cross-polarization (CP). These new NMR techniques allowed us to investigate the structural evolution of gels under thermal treatment.

2.131 Solid State ^{29}Si NMR Study of Polycondensation During Heat Treatment of Sol-Gel Silicas

Solid state MAS and CP-MAS ^{29}Si NMR spectroscopy was used to monitor polycondensation in alkoxide derived silica gels during thermal treatment from 25° to 800°C . Gels prepared from tetramethylorthosilicate under both neutral and basic conditions were studied, and differences in the evolution of chemical structure during thermal treatment are readily observed by NMR. As thermal treatment proceeds the extent of condensation parallels the BET surface area. For uncatalyzed gels, the amount of crosslinking increases, and the BET surface area decreases on each step of heating through 800°C . The base catalyzed gel depolymerizes slightly on heating from 150° to 450°C , accompanied by a slight increase in BET area, then undergoes extensive crosslinking on heating from 450° to 800°C , with a large decrease in surface area. After heating to 800°C both gels have similar degrees of crosslinking and surface area.

2.132 Solid State ^{29}Si and ^{11}B NMR Studies of Sol-Gel Derived Borosilicates

Gels in the system $\text{SiO}_2-\text{B}_2\text{O}_3$ were prepared from metal alkoxides. The structural evolution of these gels as a function of thermal treatment was studied by high field ^{29}Si and ^{11}B NMR spectroscopy, using magic angle spinning. The results corroborate earlier work on this system using infrared spectroscopy to follow the formation of borosiloxane bonds during heat treatment. While incorporation of boron into the silica backbone is negligible in gels dried at room temperature only, thermal treatment drives the borosiloxane bond formation with removal of excess water. Initial boron incorporation involves the formation of terminal $=\text{B}-\text{O}-\text{Si}^-$ groups with tetrahedral boron environments. Further heating causes the condensation of boron into symmetric trigonal $=\text{B}-\text{O}-\text{Si}^-$ sites. Boron is fully incorporated by 450°C . In addition to the symmetric trigonal boron environment of borosiloxane bonds, a small signal is also observed from ^{11}B nuclei in asymmetric trigonal environments in the gels heated to $\geq 450^\circ\text{C}$, presumably due to the formation of borate chains ($=\text{B}-\text{O}-\text{B}=$) which were previously observed with infrared spectroscopy.

2.133 Solid State ^{27}Al and ^{29}Si NMR Study of Sol-Gel Derived Alumino-silicates and Sodium Aluminosilicates

Solid state ^{27}Al and ^{29}Si NMR was used to examine the structures of aluminosilicates and sodium aluminosilicates prepared by the sol-gel method from metal alkoxides. In contrast to the borosilicate system, where B-O-Si bonds are not formed until heat treatment above 150°C , Al-O-Si formation appears complete upon gelation. Aluminum occupies tetrahedral $[\text{AlO}_4]^-$ sites in the polymer network and octahedral $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ (or similar) sites in the interstices for charge balance. When sodium is added as a counter ion, the octahedral aluminum is converted to tetrahedral aluminum in the oxide network. In gels of high aluminum content prepared from $(\text{Bu}^\text{SO})_2\text{Al-O-Si}(\text{OEt})_3$, some aluminum in five coordinate environments is also observed. All gels remain amorphous on heating through 800°C .

2.14 NMR and Raman Study of the Effect of Fluoride on the Sol-Gel Process

Natural abundance ^{29}Si NMR spectroscopy and laser Raman scattering experiments were employed to investigate the effects of fluoride ion on the gelation process in tetramethylorthosilicate at $\text{pH} = 6.4$. In addition, the BET method was used to carry out the pore analysis of the dried gels. Both the NMR and Raman data show that the presence of fluoride anions not only accelerates the gelation process but leads to a different polymerization process. The condensation proceeds via the formation of higher branched polymers, and the dimers and trimers do not play a significant role in the polymerization process. A high percentage of organic $-\text{OCH}_3$ groups is present in the silicon network at the gelation point. The pore analysis of dried gels shows that the fluoride ion leads to the formation of a loose and relatively open silica network with a large fraction of mesopores.

2.15 A SANS Study of the Effect of Catalyst on the Growth Process of Silica Gels

Small angle neutron scattering (SANS) experiments have been employed to investigate the structural evolution of uncatalyzed and fluoride catalyzed tetramethoxysilicate $\text{Si}(\text{OCH}_3)_4/\text{CH}_3\text{OH}/\text{H}_2\text{O}$ solutions from the sol to the gel state. The F^- anion has been shown to be one of the most effective catalysts for the polycondensation of silica gels. The analysis of the Guinier and Porod regions of the scattering curves yields valuable information about the particle size, the structural evolution and the growth process of these systems. The theoretical concepts of percolation and fractal geometry are applied to interpret the experimental results and to compare them with computer simulations for different growth processes in order to ascertain the origin of the developing random polymer network structure. The effects of adding a strong nucleophilic catalyst, such as NaF , on the structural properties and the growth mechanism of the silicon polymer in the course of the sol-gel transition is discussed.

2.16 The Pore Morphology of Fluoride Catalyzed Gels

The fluoride-anion has been shown to be one of the most effective catalysts in accelerating the polycondensation of alkoxide-derived silica gels. A detailed pore analysis study has been employed to investigate the effect of NaF on the pore structure of the resulting xerogels and its evolution during thermal heat treatment up to 800°C. Addition of NaF to tetramethylorthosilicate-sols leads to an increase in average pore size, and the pore size distribution becomes narrower. By changing the fluoride concentration and the heating temperature, the surface properties of the xerogels can be tuned over a wide range. The possible application of the F⁻ anion catalyzed sol-gel process to prepare porous host materials for the studies of fluids in restricted geometries is also discussed.

2.17 The Structural and Dynamical Properties of the Sol-Gel Transition

In the course of the experiments discussed in Sects. 2.14 - 2.16, we realized that there is a great need to provide more information on the gelation point and to search for more quantitative ways to determine the gelation time. The most common way of determining the gelation time is to observe when the meniscus of a sol in a container no longer remains horizontal when the container is tilted. This method also used in our experiments is somewhat arbitrary because we recognize that the gelation time depends on the volume of the sample. Sometimes a certain viscosity value, say 10⁴ Poise, is used as an indication of the gelation point.

This provided motivation for our very recent work still in progress aimed at a better definition of the gelation point. Various experimental techniques, as listed in Table 1, were employed in these experiments dealing with microscopic and macroscopic characterization of the gelation point.

Table I. Experimental Techniques Used to Study the Gelation Point

NMR Relaxation Times
Fluorescence Polarization
Turbidity
Low Frequency Raman Spectra
Static and Dynamic Light Scattering
Shear Viscosity

Also from a theoretical point of view, the nature of the sol-gel transition is a subject of extensive discussion. A gelling solution represents a unique state of matter because it is neither liquid nor solid, but rather is in transition between these two states.

We carried out viscosity, small angle neutron-scattering (SANS), NMR-, fluorescence polarization and dynamic light scattering (DLS) experiments on the polycondensation of TMOS, which lead to a detailed understanding of the macroscopic and microscopic structural and dynamical properties in course of the sol-gel transition. The experimental results are compared with growth models for the polymerization process and with recent theories for the gelation threshold.

2.2 Supercooled Viscous Liquids

2.21 Self-Diffusion in Compressed Highly Viscous Liquid 2-Ethylhexylbenzoate

We have recently reported the results of a ^1H NMR study of self-diffusion in 2-ethylhexylbenzoate (2 EHB) ($\text{C}_6\text{H}_5\text{COOCH}_2\text{CH}(\text{CH}_2\text{CH}_3)(\text{CH}_2)_3\text{CH}_3$) over a wide range of temperatures (-20 to 100°C) and pressures (1 bar to 4500 bar). The results were of intrinsic interest as the study utilized two different NMR methods to obtain self-diffusion data over the wide range of fluid viscosities accessible (1 to approximately 90,000 cP). The resultant diffusion coefficients (D) of the system ranged from around 10^{-5} to $10^{-10} \text{ cm}^2\text{s}^{-1}$, which to the best of our knowledge is an unprecedented range to be directly measured for a single fluid system. This data, combined with the corresponding density and viscosity values, presented the opportunity to analyze the transport properties of this fluid using available theories of diffusion in liquids over a very wide range of fluid states. Characterization of the degree of the coupling between the rotational and translational motions in 2EHB and the behavior of this coupling with density provided the motivation for the use of the Rough Hard Sphere (RHS) model for diffusion as developed by Chandler. In addition, the wide range of fluidity covered in this study enabled us a test of the Stokes-Einstein relationship over five orders of magnitude.

The RHS model indicates a high degree of rotational-translational coupling which increases as density increases. The non-spherical shape and conformational flexibility of the molecule is proposed as the cause of this behavior. The Stokes-Einstein equation is found to hold over five orders of magnitude changes in self-diffusion and viscosity.

2.22 Selectively Deuterated Isopropylbenzene and Toluene

The deuterium spin-lattice relaxation times, viscosities, and densities have been measured as a function of temperature and pressure for several supercooled viscous fluids, but in particular isopropylbenzene- d_5 (selectively deuterated at the ring positions) and toluene- d_8 , in order to investigate the limitations of the modified Debye equation in describing the microscopic behavior of these systems. While the question of the adequacy of the modified Debye equation was not resolved, it was shown that the rotational-translational coupling parameter, κ , is not a pressure independent quantity. Also, it was proposed that isopropylbenzene reorients anisotropically with essentially no axis of unhindered reorientation, and that the coupling parameter for the overall reorientation increase with increasing density. In the case of a symmetric molecule like toluene, which possess an axis of symmetry for relatively unhindered reorientations, the coupling parameter decreases with increasing density.

In the case of isopropylbenzene- d_5 , it has been suggested that under higher density conditions one symmetry axis' reorientations become favored compared to the other axes. As a result, the reorientational correlation time associated with the most hindered rotation will have a stronger density dependence compared to the favored rotation. In order to confirm the results outlined above, it was necessary to measure the deuterium spin-lattice relaxation times of monodeuterated isopropylbenzene and toluene at the para positions. Since the relaxation of a deuterium at this position reflects the most hindered reorientations, or

motion that requires the largest minimum volume for reorientation, we compared the density dependence of the coupling parameter for reorientations perpendicular to the symmetry axis of each molecule to that of the overall reorientations.

Since the isothermal plots of τ_0 versus η/T for isopropylbenzene-d1 and isopropylbenzene-d5 were almost identical, the nature of the density dependence of κ is the same for both analogs, and the difference between the two κ 's at constant density is relatively small. Therefore, it was safe to assume that the τ_0 versus η/T isotherm for isopropylbenzene-d5 very adequately reflects the density dependence for the overall motions in the molecule, which also confirmed the interpretation that isopropylbenzene reorients anisotropically and has no unhindered axis of reorientation.

2.23 Dipole Moment Effect on the Hydrodynamic Behavior of Cyclic Carbonate Liquids

In connection with previous studies of viscous fluids, we decided to investigate the effect of a strong dipole on the coupling between rotational and translational motions. In all the systems studied so far in our laboratory, we found that the molecular shape effects play the major role in determining the nature of the rotational-translational coupling. The three molecules in this study were 4-methyl-1,3-dioxolan-2-one (propylene carbonate), 4-chloro-1,3-dioxolan-2-one (chloroethylene carbonate), and 4,5-dichloro-1,3-dioxolan-2-one (dichloroethylene carbonate). The dipole moments of each molecule are 4.94×10^{-18} , 3.99×10^{-18} , and 3.44×10^{-18} e.s.u. respectively. Like the earlier studies, we deuterated these molecules at the ring positions and obtained the reorientation correlation times from the deuterium T_1 measurements.

Cyclic carbonates form an ideal group to investigate a dipole effect for three reasons. First, the size and shape of two of the molecules are identical, and the third molecule is similar. Second, the magnitude of their dipoles can be varied by changing the functional group on the fourth or fifth carbon in the ring. Third, they exhibit a tendency to supercool and therefore, a wide range of viscosities can be covered during the experiment. The deuterium spin-lattice relaxation times and shear viscosities of the carbonates were measured over the temperature range from -20°C to 50°C and pressures from 1 bar to 3 kbar.

It was established from previous studies that the Debye equation is successful in providing the link between reorientational correlation times and shear viscosity in supercooled viscous fluids as long as constant density conditions are maintained. The present study of the cyclic carbonates supported this conclusion as well as providing new information on the nature and relationship of the rotational-translational coupling with the strength of a permanent dipole in a molecule.

To our surprise, we found that the permanent dipole plays a role in determining the rotational-translational coupling in the viscous cyclic carbonate liquid studied. Propylene carbonate and chloroethylene carbonate have identical shape and size, but due to their differing dipole moment, their hydrodynamic behavior is different. This result motivated

us to plan additional systematic measurements on model compounds, both by NMR and laser Raman scatter experiments to explain this unexpected behavior in terms of theoretical models.

2.3 Thermotropic Ionic Liquid Crystals

2.31 X-Ray Study of Short-Chain Alkanoates

In our previous studies of anhydrous short-chain sodium alkanoates in the neat phase, we have noted the effect of anion size and shape on the motions of both anion and cation, the quadrupole coupling constant of ^{23}Na , the smectic domain size, and the order parameter. In order to understand trends in these properties we made assumptions about physical parameters such as lateral packing area. The purpose of the recent study was to determine the crystal structure of these alkanoates, as a starting point for the understanding of the mesophase structure, and to extend our knowledge of the thermal evolution of the short-chain alkanoates from the crystalline state to the neat phase. We show that the lateral packing area and the chain tilt observed in the crystalline solid correlate with properties of mesophase.

Alkali metal alkanoates do not readily form crystals large enough for single-crystal X-ray structure determination. We have had to rely upon powder diffraction data, which while more ambiguous than single-crystal data, can provide reasonable cell constants. X-ray diffraction was also used to measure bilayer spacings as a function of temperature in the solid and neat phases.

In our X-ray diffraction studies of spatial parameters of short-chain sodium alkanoates, we have found some close correspondence between the room temperature crystal structure and mesophase properties. The size of the ^{23}Na quadrupole coupling constant, which is expected to depend positively upon the lateral packing area in the mesophase, was found to be related to the room temperature lateral packing area. Bilayer spacings were found to change relatively little over the temperature range of 25-300°C, spanning several phases. We conclude that the neat phases of short-chain alkanoates resemble their crystalline phases to a greater extent than do long-chain alkanoates. This difference in behavior may be due to the reduced influence of thermal agitation for shorter chains.

Our conclusion is further supported by the fact that the lateral packing areas in sodium n-butyrate and sodium isovalerate increase by only about 25% from the room temperature crystal to the neat phase, as compared to the near doubling of the lateral packing area in long-chain n-alkanoates ($n_c \geq 12$). High temperature density measurements of other short-chain alkanoates would be useful in determining their lateral packing areas in the neat phase, in order to establish with greater certainty whether the ionic double layer remains, or is replaced by some other structure at elevated temperatures.

2.32 Calculation of Sodium-23 Quadrupole Coupling Constant in Lamellar Phases of Sodium Alkanoates

The ^{23}Na quadrupole coupling constants (QCC) were calculated for a quasi-crystalline model of the neat phase of anhydrous amphiphiles. The magnitude of the QCC in short-chain sodium alkanoates and its dependence on the lateral packing area of the polar heads was accurately predicted by assuming the charges to lie in a double-layered square array of interdigitated ion pairs.

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"Kinetics and Mechanism of Sol-Gel Polymerization," Jiri Jonas, Ultrastructure Processing of Ceramics, Glasses and Composites, Ed. L. L. Hench and D. R. Ulrich (J. W. Wiley, N.Y.), 1986.

"NMR, Raman Study of the Effect of Formamide on the Sol-Gel Process," I. Artaki, M. Bradley, T. W. Zerda, J. Jonas and G. Orzel and L. L. Hench, Ultrastructure Processing of Ceramics, Glasses and Composites, Ed. L. L. Hench and D. R. Ulrich (J. W. Wiley, N.Y.), 1986.

"Study of Polymerization Processes in Acid and Base Catalyzed Silica Sol-Gels," T. W. Zerda, I. Artaki and J. Jonas, J. Non-Crystalline Solids, 81, 365 (1986).

"Solvent Effects on the Condensation State of the Sol-Gel Process," I. Artaki, T. W. Zerda and J. Jonas, J. Non-Crystalline Solids, 81, 381 (1986).

"High Pressure in Chemical Kinetics," J. Jonas in Proc. X AIRAPT International High Pressure Conference on Research in High Pressure Science and Technology, held in Amsterdam, July 1985, Physica, 139 & 140B, 673 (1986).

"Thermotropic Ionic Liquid Crystals V. Deuterium NMR Study of Sodium n-Alkanoates," M. L. Phillips, T. M. Barbara, S. Plesko and J. Jonas, J. Chem. Phys., 84, 5143 (1986).

"Spectroscopic Investigations of Borosiloxane Bond Formation in the Sol-Gel Process," A. D. Irwin, J. S. Holmgren, T. W. Zerda and J. Jonas, Journal of Non-Crystalline Solids, 89, 191 (1987).

"Thermotropic Ionic Liquid Crystals VI. Structural Parameters of Solid and Liquid Crystal Phases of Anhydrous Short-Chain Sodium Alkanoates," M. L. Phillips and J. Jonas, Liquid Crystals, 2, 335 (1987).

"Thermotropic Ionic Liquid Crystals. VII. Calculation of Sodium-23 Quadrupole Coupling Constants in Lamellar Phases of Sodium Alkanoates," M. L. Phillips and J. Jonas, J. Chem. Phys., 86, 4294 (1987).

"Nuclear Magnetic Resonance and Laser Scattering Techniques at High Pressure," Jiri Jonas, R. van Eldik and J. Jonas Eds., High Pressure Chemistry and Biochemistry, pp. 193-235 (1987), NATO ASI, Series C, Vol. 197.

"Solid State ^{29}Si NMR Study of Polycondensation During Heat Treatment of Sol-Gel Derived Silicas," A. D. Irwin, J. S. Holmgren and J. Jonas, Materials Letters, 6, 25 (1987).

"NMR Studies of Mixed Alkoxide Systems," J. Jonas, A. D. Irwin and J. S. Holmgren, Third International Conference on Ultrastructure Processing of Ceramics, Glasses and Composites, Ed. J. D. Mackenzie and D. R. Ulrich (J. W. Wiley, NY), 1987.

"Solid State ^{29}Si and ^{11}B NMR Studies of Sol-Gel Derived Borosilicates," A. D. Irwin, J. S. Holmgren and J. Jonas, Journal of Non-Crystalline Solids, 101, 249 (1988).

"Self-Diffusion in the Compressed, Highly Viscous Liquid 2-Ethylhexyl Benzoate," N. A. Walker, D. M. Lamb, S. T. Adamy, J. Jonas, and M. P. Dare-Edwards, Journal of Phys. Chem., 92, 3675 (1988).

" ^{27}Al and ^{29}Si NMR Study of Sol-Gel Derived Aluminosilicates and Sodium Aluminosilicates," A. D. Irwin, J. S. Holmgren and J. Jonas, Journal of Materials Science, 23, 2908 (1988).

"The Effect of Fluoride on the Sol-Gel Process," R. Winter, J.-B. Chan, R. Frattini and J. Jonas, J. of Non-Crystalline Solids, 105, 214 (1988).

"The Pore Morphology of Fluoride Catalyzed Xerogels," J.-B. Chan, D.-W. Hua, R. Winter and J. Jonas, J. of Materials Research, in press.

"A SANS Study of the Effect of Catalyst on the Growth Process of Silica Gels," R. Winter, D.-W. Hua, P. Thiagarajan and J. Jonas, J. of Non-Crystalline Solids, in press.

"The Structural and Dynamical Properties of the Sol-Gel Transition," R. Winter, D.-W. Hua, X. Song and J. Jonas, ILL Workshop "Dynamics of Disordered Materials," September 1988, Grenoble, France.

4. Ph.D. Theses Supported by the Grant AFOSR 85-0345

Alan Dale Irwin, "Multinuclear NMR Investigations of Sol-Gel Systems" 1987

Margaret Levin Phillips, "Structure and Dynamics of Thermotropic Liquid Crystalline and Solid Phases of Sodium Alkanoates" 1987

Michael John Welsh, "High Pressure N.M.R. Studies of Supercooled Viscous Fluids" 1987

5. Research Personnel

5.1 Senior Personnel

Dr. I. Artaki	Dr. N. A. Walker
Dr. R. Frattini	Dr. R. Winter
Dr. J. S. Holmgren	Dr. T. W. Zerda
Dr. S. Plesko	

5.2 Junior Personnel

S. T. Adamy	A. D. Irwin
J.-B. Chan	M. L. Phillips
D.-W. Hua	M. J. Welsh